



UTILIZATION OF HYDROXIDE COMPOUND AS CO₂ ABSORBENT FOR MEASUREMENT OF CARBON-14 IN CORAL REEF SAMPLE FROM SPERMONDE ARCHIPELAGO

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ABSTRACT

The use of hydroxide compounds as CO₂ absorbents for Measurement of Carbon-14 in Coral Reef Sample from Spermonde Archipelago. This research aimed to determine the age of coral reef sample of Spermonde Archipelago by measuring the activity of carbon-14 using the method Liquid Scintillation Counting (LSC). The coral reef sample was collected in Langkai Island. The research was conducted by following steps of sample preparation, the CO₂ absorption using the hydroxide solutions (KOH and NaOH). The measurement of the carbon-14 activities was performed using the Liquid Scintillation Counter (LSC) Hidex 300 SL. The research results indicated that the absorption capacities of KOH and NaOH were 0,450 and 0,425 mol CO₂/mol hydroxide respectively. The specific activity of coral reef sample using absorbent KOH and NaOH were 14.51; and 14.57 DPM/g C, respectively. The age of coral reef sample, which was calculated based on the specific activity values using the absorbents KOH and NaOH were 436.13; and 403.61 years, respectively.

Keywords: LSC, Carbon-14, CO₂ Absorption, Hydroxide, Spermonde

1. INTRODUCTION

Coral reefs are one of the sea creatures have a life time or a very long age. With the support of allegations some geologists who say that 75% of all coral reefs formed during the Pleistocene^[6].

Determination of the age of the coral reefs in the waters has a huge benefit in studying the geography of marine origin such coral samples to trace and study the formation sector in coastal rock formations, especially if an area is an area of islands with coral reef biodiversity levels are very high. As Spermonde archipelago which has a fairly high coral diversity, therefore, Spermonde an ideal location to perform marine research both involving biology, chemistry, geology, sociology, archeology, and culture of which are summarized in the context of Indonesian Maritime Continent^[10].

Radioisotope of ¹⁴C with a half-life of 5730 years is one of the common radioisotope used for determining the age of a sample which contains carbon such as coral reefs, sediment, groundwater, and others. Determination age of the coral reefs can be done by using radiocarbon dating method, a method that is based on the calculation of the ¹⁴C activity was contained in a carbon sample. The value of this activity then converted into age when compared with the reference standard modern^[7].

Method of age determination using ¹⁴C which has been done by counting C₆H₆ with the liquid scintillation counter. However, this method is done with sufficient complicated sample preparation, time, and requires consideration of the necessary technical skills that are



considered uneconomical and inefficient [7].

Against this background, applied the new method is absorption of CO_2 as an alternative method that is began to be used in the last two decades [7][8].

CO_2 absorption approach is based on the basic principle is the same as the benzene-LSC method. The main difference is that the CO_2 produced from the sample is absorbed directly into the appropriate cocktail with high CO_2 affinity and directly counted by LSC without further changes. The method is simple, safe, and results of significantly reducing analysis time and cost compared to conventional methods [2]. Hydroxide compounds, such as KOH and NaOH can be absorbent alternative in radiocarbon measurements on samples of coral reefs by LSC through direct absorption of CO_2 pretreatment. Research conducted by Jauhari (2013), using KOH as an absorber obtained specific activity of ^{14}C in samples of coral reefs in the archipelago Spermonde was 14.11 ± 0.5 dpm / grC and 669.484 ± 20 years old.

Carbon-14 analysis which is correct and accountable is the most important factor in assessing the status of a coral reef. Therefore, in this study will be conducted to determine the capacity of hydroxide compound (KOH and NaOH) as CO_2 absorbent for radiocarbon measurements in samples of coral reefs sample.

2. MATERIAL AND METHOD

Materials

The materials of this study was 30% H_2O_2 , HClO_4 1 N, 1 N NaOH, Hydroxide compound, N_2 gas HP (High Purity), 10%

HCl, AgNO_3 , silica gel, marble, aqua light, LLT, filter paper, distilled water and coral reefs.

Apparatus

Preparation tool in form of round-bottom flask, impinge, funnel, absorption column, glass cup, mortar, oven, hammer and tools glasses commonly used in laboratories as well as β radiation count tool of carbon-14 sample is LSC Hidex 300 SL.

Sampling

Coral sample taken at seawater near one of the islands in the Spermonde Archipelago, which is in Langkai Island at a depth about 4-5 m. Langkai Island located on coordinate S: $05^\circ 01' 47,055''$ E: $119^\circ 05' 50,272''$. Marble from Maros region is used as the Background Materials.

Physical and Chemical Cleaning

Cleaning methods are designed to remove contaminating carbon sources that accumulate both while the specimen is on the sea floor and while it is stored on land after collection. Water rinses and scrubbing with a brush remove sediment from inside the coral and between the septa. Samples are then immersed in a 1:1 mixture of 30% H_2O_2 and 1N NaOH and ultrasonicated for 15 minutes. However, this process often leaves a brownish/orange organic stain on the CaCO_3 . Quick dips (30 seconds to 2 minutes) in a 1:1 mixture of 30% H_2O_2 and 1N HClO_4 effectively remove this stain. After the dilute perchloric step, samples are rinsed thoroughly with clean distilled water. For the second acid wash,

pre-weighed samples are dipped into 6N HCl for 15–60 seconds followed by rinses in two separate beakers of distilled H₂O. After drying for several minutes in a 60 °C oven, the samples are cooled and reweighed to determine the percent of sample removed. Samples are then crushed in an agate mortar and pestle to facilitate dissolution in the reaction flasks ^[1].

Carbon Dioxide Absorption

Dried coral were transferred to flask that connected to a separation funnel as hydrochloric acid reservoir. Prior to carbon dioxide absorption, the nitrogen gas was streamed along the system. Solution of 10% HCl was added by drops to the sample until bubbles formed (Fig.1). Gas is channeled into an impinger contains 40 mL of KOH or NaOH as CO₂ absorbent after passed acid trap and water trap. The process was stopped when the gas not formed by adding the hydrochloric acid. Concentration of CO₂ absorbed was quantified from the difference of weight before and after absorption process

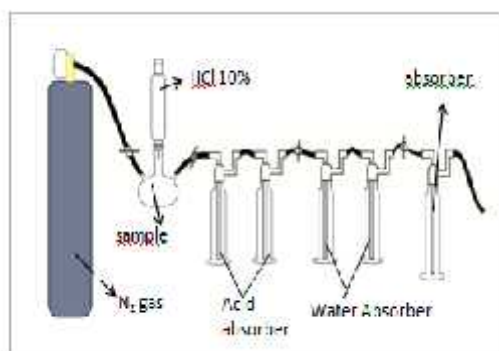


Figure 1. Design of absorption system of carbon dioxide from coral sample

The same method is used to absorb CO₂ from marble for use in the measurement of the Background.

Determination of Total Carbon

Next step is the determination of total carbon. Carbonate solution was pipetted to 10 mL, further dilution with distilled water. Titration performed with 5 M HCl and the addition of MO indicator. Titration was conducted to determine the total base. Then the solution was filtered and the filtrate was re-added with 10% BaCl₂. The filtrate was pipetted 10 mL and added to the erlenmeyer and added with a few drops of indicator PP, then back titrated with HCl 5 M. The titration is then performed to determine the total alkaline OH.

Carbon-14 Counting

Approximately 8 mL of sample or background mixture with 12 mL scintillator in 20 mL vial. The mixture was homogenated by shaking and saved from light exposure, and then lied on 20 mL vial plate tray. Counting the sample as protocol LSC Hidex 300 SL and it was counted at 2-150 minutes in range.

3. RESULT AND DISCUSSION

Physical and Chemical Cleaning

Coral sample that have been physically and chemically cleaned looked clean and white. The chemical cleaning removed impurities and carbon source on the surface up to 8.63 %. The result of these experiments are not much different from the result of deep-sea coral sample cleanup was done by Adkins et al.(2002) and Maming et al. (2014). The missing part of the sample is a natural contaminant that accumulates over the coral reef waters and dissolved matrix surface.

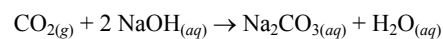
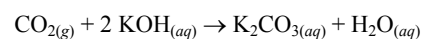
Carbon Dioxide Absorption

The main component coral as carbonate that have been grinded are separated by reaction with hydrochloric acid, based on the reaction:



Carbonate in this reaction is released as CO_2 gas when the sample react with acid. Carbon dioxide is absorbed by

hydroxide compound (KOH and NaOH) trough chemical reaction as carbonate, based on the reaction:



The correlation between weight of CO_2 and weight sample is showing on the figure 2.

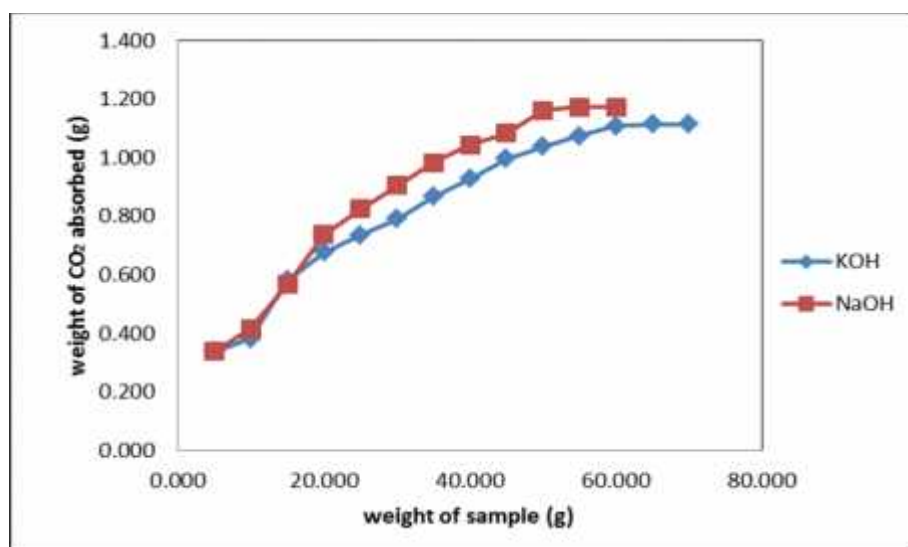


Figure 2. Correlation between weight of sample with amount of CO_2 absorbed by KOH and NaOH

Table 1. The optimum amount of CO_2 absorbed by KOH and NaOH

Absorbent	Amount of CO_2	
	Weight of CO_2 (g)	mol CO_2 / mol hydroxide compound
KOH	0.1728	0.450
NaOH	0.1632	0.425

The amount of CO_2 absorbed by the absorbent solution, can be known by determining the total carbon through titration method. The optimum amount of CO_2 absorbed by KOH and NaOH are listed on the table 1.

Carbon-14 Counting

The results of measurements of ^{14}C activity measured on the instrument is expressed in units of Count Per Minute (CPM) which shows the number of β particles produced from ^{14}C in coral

sample in every minute, and the activity of coral sample is expressed in units Disintegration Per Minute (DPM) which shows the actual number of atoms in the ^{14}C decays coral samples in every minute.

The relationship between the value of DPM and the value CPM is expressed as a form of efficiency in units of enumeration which stated Triple Double Coincidence Ratio (TDCR).

Measurement of Carbon-14 activity of

KOH and NaOH solution also investigated as background. Besides the use of absorbent solution itself as the background, in this research also using marble as a source of CO_2 background ^[2] ^[8]. Marble is a carbon source with old age that is considered to contain carbon-14 with very low activity.

Comparison of activity measurements of carbon-14 in the sample and background are shown in Figure 3 and 4.

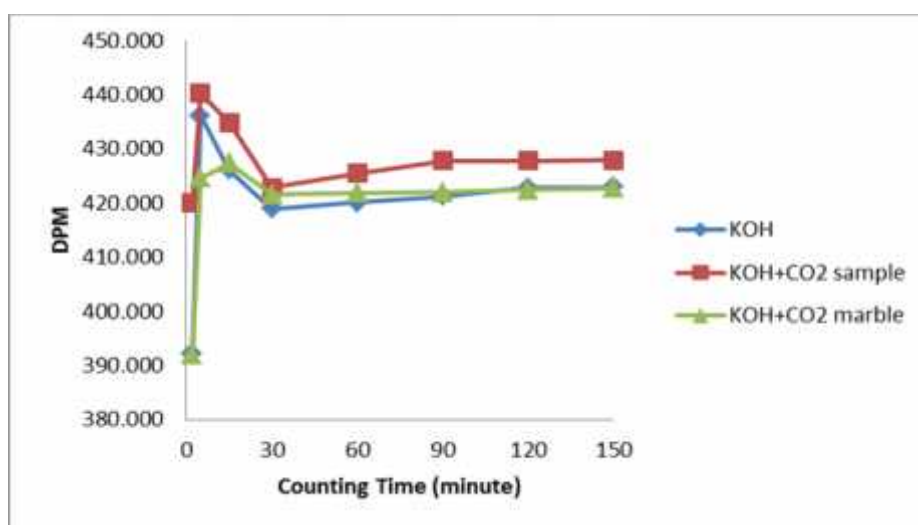


Figure 3. Comparison of activity measurements of carbon-14 in the sample and background using KOH absorbent

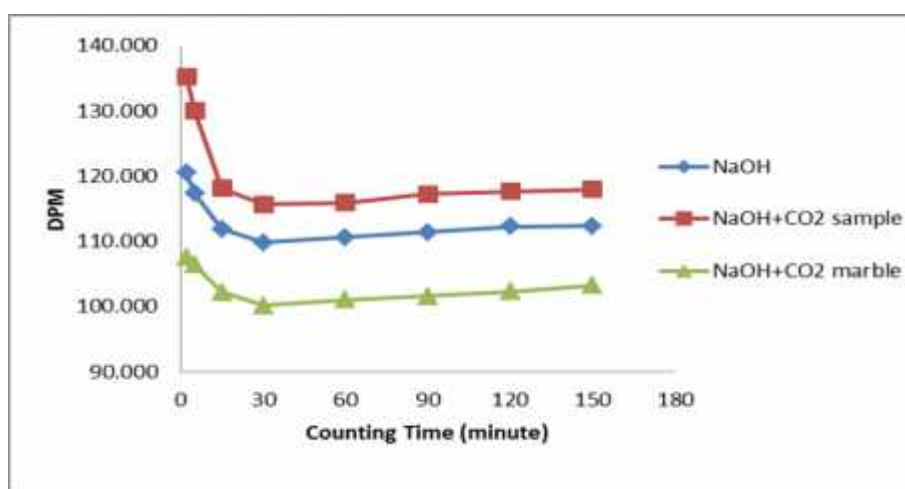


Figure 4. Comparison of activity measurements of carbon-14 in the sample and background using NaOH absorbent



In figure 3 and 4 shows that the measurement both of background, the absorbent itself and marble showed lower activity than the sample. Therefore, both

of background are used to correct activity of carbon-14 from sample.

Comparison of activity measurements of carbon-14 in the sample and background are shown in Table 2.

Table 2. Activity of ^{14}C of sample and background

Absorben	CPM			DPM			TDCR		
	Sample	Absorbent	Marble	Sample	Absorbent	Marble	Sample	Absorbent	Marble
KOH	288.288	291.182	289.182	422.398	419.890	420.978	0.682	0.693	0.687
NaOH	63.284	62.522	56.090	109.942	107.114	105.384	0.572	0.584	0.533

From Table 2 shows that the efficiency of the order of enumeration (TDCR) using absorbent KOH and NaOH are $\text{KOH} > \text{NaOH}$.

Specific Activity and Coral Age Estimation

Determination of specific activities are needed in order to determining the age of the sample. The specific activity is the basis for calculating the age of the coral

sample obtained from the activity value of DPM divided by the total carbon weight of sample mixed with scintillator. The value of specific activity expressed in units of DPM per unit mass. Specific activity data of coral sample is shown in Table 3. The specific activity value (A_s) shows the actual number of ^{14}C atoms which disintegration per minute (dpm) in each gram of the element carbon.

Table 3. Specific activity data of coral samples from Langkai Island

Absoben	Background	DPM	C-total (g)	As (DPM/gC)	As C-14 life*
KOH	KOH	2.508	0.1728	14.51	15.30 ± 0.1
	KOH+CO ₂ marble	2.506	0.1728	14.50	15.30 ± 0.1
NaOH	NaOH	2.378	0.1632	14.57	15.30 ± 0.1
	NaOH+CO ₂ marble	2.352	0.1632	14.41	15.30 ± 0.1

Based on the following equation can be obtained The Age estimation of coral sample is obtained based on the specific activities that have been obtained previously.

$$t = \frac{t_{1/2}}{\ln 2} \ln \frac{A_0}{A_t}$$

Where:

A = Radioactive ^{14}C in the sample



A_o = Radioactivity of ^{14}C isotopes in living organisms $15.3 \text{ DPM} / \text{gC}^5$

$t_{1/2}$ = half-life = 5730 years

$\ln 2$ = 0.693

The age of coral sample calculated from the specific activity using absorbent KOH and NaOH was 436.13 ± 159 and 403.61 ± 74 years respectively.

4. CONCLUSION

In this study concluded that the absorption capacity of KOH and NaOH was specific activity of coral sample using absorbent KOH and NaOH was 0.450 and 0.425 mol CO_2 /mol hydroxide respectively. The specific activity of coral reef sample using absorbent KOH and NaOH was 14.51; and 14.57 DPM/g C, respectively. The age of coral reef sample calculated from the specific activity using absorbents KOH and NaOH was 436.13 ± 159 and 403.61 ± 74 years respectively.

REFERENCES

- [1] Adkins, J.F., Griffin, S., Kashgaria, M., Cheng, H., Druffel, E.R.M., Boyoyle, E.A., Edwards, R.L., Shen, C.C. (2002) Radiocarbon Dating of Deep-Sea Corals. *Radiocarbon*. 44 (2) : 567-580.
- [2] Canducci, C., Bartolomei, P., Magnani, G., Rizzo, A. (2013) Upgrade of the CO_2 Direct Absorption Method for Low Level ^{14}C Liquid Scintillation Counting. *Radiocarbon*. 55 (2-3): 260-267.
- [3] Faurescu, I., Varlam, C., Stefanescu, I., Cuna, S., Vagner, I., Faurescu, D., Bogdan, D. (2010) Direct Absorption Method and Liquid Scintillation Counting For Radiocarbon Measurements in Organic Carbon from Sediments. *Radiocarbon*. 52 (2-3): 794-799.
- [4] Libby, W.F.(1960) Radiocarbon Dating. Nobel Lecture. Elsevier Publishing Company: Amsterdam.
- [5] Maming, Noor, A., Zakir, M., Raya, I., Jauhari, Kartika, S.A. (2014) Application in Liquid Scintillation Method on Carbon Dating in Determination of Coral Ages from Spermonde Archipelagos. *Marine Chimica Acta*. 15 (1): 31-35.
- [6] Rositasari, R., 1998, Aspek Ekologi dan Sejarah Pembentukan Terumbu Karang, *Balitbang Oseanografi, Puslitbang Oseanologi-LIPI*, Jakarta, 13 (3, 4): 1-9.
- [7] Satrio and Abidin, Z (2007) Perbandingan Metode Sintesis Benzena Dan Absorpsi CO_2 Untuk Penanggalan Radioisotop ^{14}C . *Jurnal Ilmiah Aplikasi Isotop Dan Radiasi*. 3 (1): 1-34.
- [8] Varlam, C, Stefanescu, I., Varlam, M., Popescu, I., Faurescu, I., 2007, Applying the Direct Absorption Method And LSC For ^{14}C Concentration Measurement In Aqueous Samples, *Radiocarbon*, 49(2), 281-289
- [9] Varlam, C., Stefanescu, I., Cuna, S., Vagner, I., Faurescu, I., Faurescu, D. (2010) Radiocarbon and Tritium Levels along the Romanian Lower Danube River. *Radiocarbon*. 52, (2-3): 783-793.
- [10] Yuliati, H., Akhadi, M. (2005) Radionuklida Kosmogenik Untuk Penanggalan. *Puslitbang Keselamatan Radiasi dan Biomedika Nuklir*. Pusat radiasiBatan